

METHOD FOR RECOVERY OF NONFERROUS, RARE AND PRECIOUS METALS FROM ROBUST MINERALS

The method is referred to hydrometallurgy process and it serves for recovery of nonferrous, rare and precious metals from robust (hard to process) minerals, which may contain natural carbon or other robust compounds.

Very frequently the well-known techniques for recovery of nonferrous, rare and precious metals from robust minerals containing carbonaceous component or other robust compounds, do not provide satisfactory performance.

First of all it stems from high resistance to oxidation and high sorption activity of carbonaceous component of the minerals involving great loss of nonferrous, rare and precious metals with solid residue of processing.

In the framework of the present method ores and concentrates containing organometallic, cluster, colloid and other chemical and composite compounds, hindering the process of useful components recovery, should be classified among technologically robust minerals.

Hence, during cyanidation of robust carbonaceous ores and concentrates, for instance, no traces of precious metals are detected in solution in some cases, i.e. precious metal complexes formed as a result of interaction with cyanide are completely adsorbed by carbonaceous component in the mineral. Cyanidation in the presence of ion-exchange resins and carbons, as well as using sorption passivators like kerosene or apolar liquids, somewhat improves the recovery of precious metals but not infrequently its processing characteristics are as low.

Methods for carbonaceous ore leaching are described in the book "Precious Metals Metallurgy" by Maslénitsky et al. published in Moscow in 1987, pages 288-291 as follows: "... in some ores carbonaceous substances feature different settling capability, which complicates largely the cyanidation process. ... During cyanidation of carbonaceous ores kinetics of precious metal transfer to solution is determined by the ratio of two opposite processes, i.e. dissolution and sorption. ... Certain rate of leaching ... promotes maximum extraction ... in the course of carbonaceous ores cyanidation. The rate of sorption depends also on carbonaceous substance surface area. Optimal degree of material grinding should be maintained. Thus, one of the methods of carbonaceous ore direct cyanidation consists in arrangement of usual cyanide process, observing the optimal degree of grinding and period of contact between the ore and cyanic solution. Another method... consists in arrangement of leaching in several successive stages with solution renewal at each stage. Adsorption capacity of carbonaceous substances may be somewhat decreased by preliminary treatment of ore using flotation oils, kerosene, bituminous coal sublimation products and some other reagents.... However, the efficiency of the method is not very high. ... Cyanidation of carbonaceous ores using water-soluble organic nitriles, their actual applications not being ultimately ascertained, is of interest. Sorption leaching proved the most efficient method for cyanidation of carbonaceous ores and concentrates ".

Attempts to reduce sorption activity of carbon-containing raw materials by thermal treatment in vacuum (for removing unsaturated oxides from carbon) failed to be widely used due to problems in hardware implementation, high costs of the process and low process performance.

In monograph "Solvents for Gold and Silver in Hydrometallurgy" by Mineev G.G. and Panchenko A.F. published by "Metallurgiya" (Metallurgy) Publishing House in 1994 in Moscow some problems arising from application of the known methods of leaching are mentioned in pages 192-205: "Bacterial leaching involves problems of intracellular metal accumulation, low performance of subsequent sorption leaching, build-up of biomass on the equipment". Leaching

by heterotrophic microorganism metabolism products and amino acid solutions yielded rather low results in reference to recovery into solution. Filtration leaching of gold-containing source materials necessitates recycling of productive solutions. That is why the latter shall be processed in situ, while methods of gold recovery from solutions shall feature high efficiency, simplicity of hardware implementation and no pollution of gold-free filters by other components. Hence, sorption biochemical leaching was chosen as the basic method for gold recovery from ores.

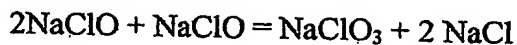
Passivation of carbon sorption activity using bacteria active life products (bacterial leaching) necessitates special fermenters for growing bacteria, fine grinding of the material, strict observance of temperature and chemical conditions, long duration of the process. In some cases, when there are great amounts of As and Sb, for instance, bacterial leaching proved impossible due to bacteria poisoning with heavy metals. Bearing in mind the above-mentioned, bacterial leaching has not been used extensively for processing robust carbonaceous minerals.

Chlorination method of precious metal recovery from ores, consisting in ore treatment by aqueous solution of hypochlorite, iron ions and acid at elevated temperature, is its immediate analog (prior art), solving the problem of precious metal recovery from robust minerals, which is described in US Patent No. 4439235 of 14.06.1982, Int.Cl.³: C22D 3/00, U.S. Cl.: 75/101 R. After filtration the solid residue is treated repeatedly by hypochlorite and iron-ion aqueous solutions at pH=7. Compounds of precious metals are extracted from liquid phase.

The prior art mentioned and the stated technical approach have the following in common: treatment of robust carbon-containing mineral with oxygen-containing oxidant and subsequent extraction of precious metal compounds from liquid phase.

Great consumption of hypochlorite for mineral oxidation, explained by the fact that hypochlorite decomposition, especially at elevated temperature, proceeds according to chlorates and chlorides formation mechanism, can be mentioned

among drawbacks of the method described. Meanwhile, hypochlorite and its disproportionation products do not take part in oxidation of precious metals and their transfer to solution:



High oxidizing activity of hypochlorites combined with their thermodynamic instability results in a very rapid decrease in effective oxidant concentration in the slurry, giving rise to high cost of processing and insufficient degree of precious metal recovery from minerals.

This invention is aimed at increasing the recovery of nonferrous, rare and precious metals from robust minerals with simultaneous reduction of processing costs.

The objective is attained, as the method for recovery of nonferrous, rare and precious metals from robust minerals envisages the processing of robust carbon-containing minerals by oxygen-containing oxidant with subsequent extraction of precious metal compounds from liquid phase, moreover, the treatment of robust carbon-containing minerals by oxygen-containing oxidant is performed in the presence of reducing agents featuring donor-acceptor properties, which are manifested in the fact that at the first stage of chemical reactions the reducing agents give their electrons to oxygen-containing oxidant and, as a result, form a stronger oxidant than the initial one, in the form of short-lived radicals and intermediate oxidation products of donor-acceptor reducing agents, which are oxidants, as well.

According to the method proposed, the treatment of robust carbon-containing minerals by oxygen-containing oxidant is realized in the presence of reducing agents featuring donor-acceptor properties. Donor-acceptor properties of the reducing agents used are pronounced in the fact that at the first stage of chemical reactions the reducing agents give their electrons to oxygen-containing oxidant and as a result form a stronger than initial oxidant, in the form of short-

lived radicals and intermediate oxidation products of donor-acceptor reducing agents, which are mild and selective oxidants.

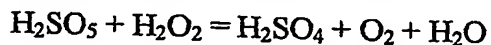
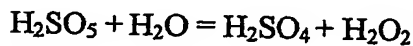
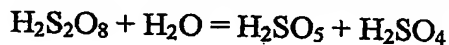
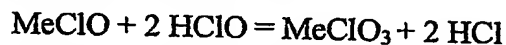
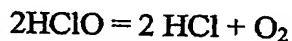
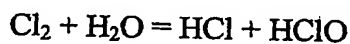
Technically, the essence of the invention proceeds from specific features of using oxygen-containing compounds as oxidants for robust minerals.

Introduction of the donor-acceptor reducing agents into hydrometallurgical process permits:

- first, directing the decomposition of oxygen-containing oxidants in line with the most favorable mechanism for oxidation of nonferrous, rare and precious metals;
- second, prolonging the action of oxidants by mediating their oxidizing potential via the reducing agents oxidation products, which are milder and more selective oxidizing agents;
- third, making use of complexing capability of the reducing agents for overcoming kinetic and electrochemical difficulties in dissolving nonferrous, rare and precious metals and stabilizing the dissolved precious metals in liquid phase;
- fourth, transforming the intermediate compounds formed as a result of oxygen-containing oxidant disproportionation into short-lived "fast radicals", permitting oxidation of organometallic, cluster, colloid and other chemical and composite compounds, which increases essentially the utilization factor of robust minerals.

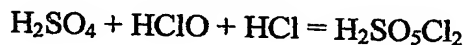
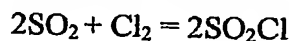
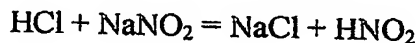
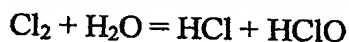
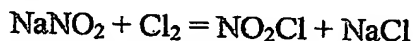
Existence of the above-mentioned mechanisms of chemical interactions is confirmed by the following theoretical and experimental data:

1) In solutions of oxygen-containing oxidants without donor-acceptor reducing agents the decomposition of oxidants proceeds by the following reactions:



It follows from the reactions presented that as a result of decomposition of oxygen-containing oxidants, not involving donor-acceptor reducing agents, the decomposition and disproportionation products are accumulated in solution along with evolution of gaseous oxygen, which are not effective oxidants under normal conditions. Accordingly, it gives rise to high consumption of oxidants and low performance of recovery process.

2) In the presence of donor-acceptor reducing agents the oxidation potential of oxygen-containing compounds is actually entirely used for the formation of short-lived radicals and reducing agent oxidation products. The following reactions take place as a result:



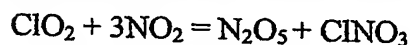
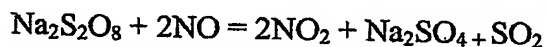
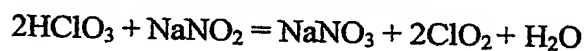
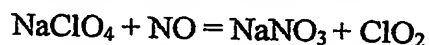
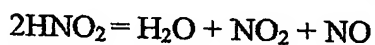
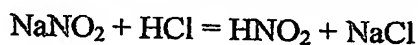
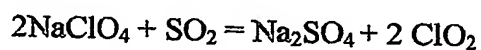
Using NaNO_2 and SO_2 by way of example, it follows from the reactions presented that interaction between the Cl_2 - HClO oxidant and donor-acceptor reducing agents gives rise to formation of many products, i.e. NaNO_3 , NOCl , NO_2Cl , HNO_2 , SO_2Cl , O_2 , $\text{H}_2\text{SO}_5\text{Cl}_2$, etc., each of them can serve an independent oxidant for nonferrous, rare and precious metals.

Meanwhile, the oxidation potentials developed by the compounds during reduction to lower valency states, fall within a wide range relative to normal hydrogen electrode. Actually all the substances feature complexing properties and form compounds with nonferrous, rare and precious metals, required for the process. The presence of various compounds featuring diverse electrochemical and complexing properties during oxidation of nonferrous, rare and precious

metals permits increasing thermodynamic probability of the metals oxidation and their transfer to solution.

Compounds of higher oxidation state, e.g. chlorates, perchlorates, persulfates, perbromates, other oxygen-containing oxidants and their derivatives have great bound chemical energy, but chemical energy cannot be used for oxidation of nonferrous, rare and precious metals owing to stability of chlorates and perchlorates as compounds and their low chemical activity.

In the invention proposed oxidants featuring the highest valency of acid residue atom, for instance, chlorates, perchlorates, persulfates, perbromates, other oxygen-containing oxidants and their derivatives are used as oxidants in the presence of donor-acceptor reducing agents. As a result, the donor-acceptor reducing agents give rise to the formation of radical, i.e. oxygen superoxide, atomic oxygen and other highly reactive compounds, including the reducing agents oxidation products, which permits effective oxidation and dissolution of nonferrous, rare and precious metals contained in the minerals, i.e.:



It becomes obvious from the reasoning above that the proposed method for recovery of precious metals differs from the known ones, as robust minerals are treated with oxygen-containing oxidants in the presence of reducing agents featuring donor-acceptor properties. Thus, the proposed method complies with the "novelty" criterion.

Comparison of the approach proposed with the prior art and other approaches in this field of engineering permitted revealing the signs, making the proposed approach different from the prior art, moreover, the differences considered are implicit, which suggests conclusion about compliance of the approach proposed with the "invention level" criterion. The approach proposed has industrial applications.

Examples of specific applications for the process proposed:

Example No. 1.

Hydrometallurgical oxidation was realized using ore featuring the following mineral composition:

a) non-metallic minerals

siderite – 18.2%, calcite – 1.0%, quartz – 8.3%, kaolin – 4.5 %,
chlorite – 1.8%, albite – 1.0%, hydromica – 1.0%, apatite – 0.3%;

b) ore mineral

goethite, limonite – 61.5%, pyrite – 1.2%, chalcopryrite – 0.85%,
bornite 0.2%, covellite 0.1%.

The ore contained gold 7.4 g/ton ore, platinum 56 g/ton ore, palladium 12 g/ton ore, and silver 150 g/ton ore, as well as copper 0.7% and cobalt 0.2%.

The ore, its amount 1 kg, was subjected to hydrometallurgical oxidation in hydrochloric acid solution, its concentration 100 g per liter, in liquid-to-solid ratio (L:S) = 3:1, at a temperature of 80°C with intense agitation.

Ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was used as oxidant in the amount providing concentration of 10 g per liter, which was introduced into the slurry immediately after heating to assigned temperature. Check sample was agitated in parallel with the basic one without addition of donor-acceptor reducing agents.

Solution containing 10 g/l of sodium nitrite NaNO_2 and 10 g/l of sodium sulfite Na_2SO_3 was introduced gradually into the basic sample. The feed rate depended

on gas evolution intensity. Altogether 100 ml of solution containing donor-acceptor reducing agents was consumed in 30 minutes. Hence, 1 gram of NaNO_2 and 1 gram Na_2SO_3 was consumed per total amount of the oxidant equal to 30 grams.

The solutions prepared and solid residue were analyzed by atomic-absorption and assay analyses for ascertaining the extraction of nonferrous and precious metals into solution.

In the check sample (without addition of donor-acceptor reducing agents) the extraction into solution made up:

Copper – 73%, cobalt 68%, silver 57%, gold 64%, platinum 31%, palladium 47% of their content in the sample.

In the sample with donor-acceptor reducing agents metal extraction into solution amounted to:

Copper – 98.5%, cobalt 97%, silver 94%, gold 98.3%, platinum 94%, palladium 97%.

The results suggest that the use of donor-acceptor reducing agents increases essentially the extraction of nonferrous and precious metals from robust minerals.

Example No. 2.

Hydrometallurgical oxidation was realized using ore featuring the following mineral composition:

a) non-metallic minerals

siderite – 12.2%, calcite – 7.0%, quartz – 37.8%, kaolin – 3.7 %, chlorite – 2.8%, albite – 2.0%, hydromica – 12.0%, apatite – 0.7%, carbonaceous matter 4.5%:

b) ore minerals

goethite, limonite – 11.5%, pyrite – 3.2%, pyrrhotine – 2.5%, arsenopyrite – 0.1%.

The ore contained gold 3.4 g/ton ore, platinum 2.6 g/ton ore, palladium 3.2 g/ton ore, and silver 5 g/ton ore.

The ore, its amount 1 kg, was subjected to hydrometallurgical oxidation in hydrochloric acid solution, its concentration 10 g per liter, at L:S = 3:1, at a temperature of 40°C with intense agitation.

Sodium hypochlorite NaClO was used as oxidant in the amount providing the concentration of 5 g/l, which was introduced into the slurry immediately after heating up to the assigned temperature. The check sample was agitated in parallel with the basic one without addition of donor-acceptor reducing agents.

Solution containing 10 g/l of sodium nitrite NaNO_2 was introduced gradually into the basic sample. The feed rate depended on gas evolution intensity. Altogether 200 ml of solution containing donor-acceptor reducing agent was consumed in 30 minutes. Hence, 2 grams of NaNO_2 was consumed per total amount of the oxidant equal to 15 grams.

The solutions prepared and solid residue were analyzed by atomic-absorption and assay analyses for ascertaining the extraction of nonferrous and precious metals into solution.

In the check sample (without addition of donor-acceptor reducing agent) the extraction into solution made up: silver 37%, gold 52%, platinum 21%, palladium 37% of their content in the sample.

In the sample with donor-acceptor reducing agents metal extraction into solution amounted to:
silver 87%, gold 92.3%, platinum 74%, palladium 87%.

The results suggest that the use of donor-acceptor reducing agents increases essentially the extraction of nonferrous and precious metals from robust minerals.

Example No. 3.

Hydrometallurgical oxidation was performed using gravity concentrate featuring the following chemical composition:

SiO₂ – 23%, Al₂O₃ – 5.6%, Fe (total) – 28%, S (total) – 36%, crystallization water – 1.34%, CaO – 1.12 %, MgO – 0.8%.

The concentrate contained gold 378 g/ton ore, platinum 47 g/ton ore, palladium 126 g/ton ore, and silver 2480 g/ton ore, as well as 3.8% of nickel and 2.4% of cobalt.

The concentrate in the amount of 1 kg was subjected to hydrometallurgical oxidation in hydrochloric acid solution, its concentration 70 g per liter, at L:S = 2:1, at a temperature of 70°C under intensive agitation.

Ammonium perchlorate (NH)₂Cl₂O₇ was used as oxidant in the amount providing concentration of 10 g per liter, and sodium iodate NaJO₃ in the amount providing concentration of 5 g per liter, were introduced into the slurry immediately after heating to assigned temperature. The check sample was agitated in parallel with the basic one without addition of donor-acceptor reducing agents.

Solution containing 10 g/l of sodium sulfite Na₂SO₃ and 5 g/l sodium thiosulfate Na₂S₂O₃ was gradually introduced in the basic sample. The feed rate depended on gas evolution intensity. In total 300 ml of solution containing donor-acceptor reducing agents was consumed in 45 minutes. So, 3 grams of Na₂SO₃ and 1.5 grams of Na₂S₂O₃ were consumed per total amount of oxidants equal to 45 grams.

The solutions prepared and solid residue were analyzed by atomic-absorption and assay analyses for ascertaining the extraction of nonferrous and precious metals into solution.

In the check sample (without addition of donor-acceptor reducing agents) the extraction into solution made up:

nickel – 63%, cobalt – 57%, silver – 48%, gold – 63%, platinum – 42%, palladium – 54% of their content in the sample.

In the sample with donor-acceptor reducing agents metal extraction into solution amounted to:

nickel – 98.5%, cobalt – 95%, silver – 89%, gold – 94%, platinum – 89%, palladium – 92%.

The results suggest that the use of donor-acceptor reducing agents increases essentially the extraction of nonferrous and precious metals from robust minerals.